

PATENT SPECIFICATION

(11) 1 523 028

1 523 028

(21) Application No. 32731/76 (22) Filed 5 Aug. 1976

(31) Convention Application No. 26221

(32) Filed 8 Aug. 1975 in

(33) Italy (IT)

(44) Complete Specification published 31 Aug. 1978

(51) INT CL² C07C 121/00

(52) Index at acceptance

C2C 200 20Y 30Y 326 360 363 36Y 47X 623 62Y 66Y MB NQ

(72) Inventors RENATO DE SIMONE
EDOARDO PLATONE and
MORELLO MORELLI

(19)

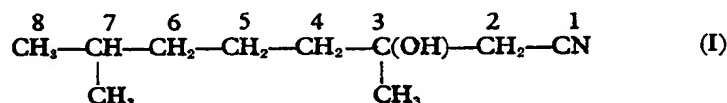


(54) NITRILE AND PRODUCTION OF NITRILES

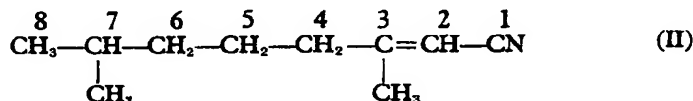
(71) We, ANIC S.P.A., an Italian company, of Via M. Stabile 216, Palermo, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to two nitriles, one of which is novel, and to their production.

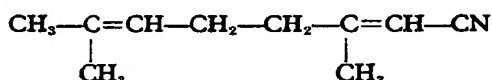
One aspect of the present invention provides 3,7-dimethyl-3-hydroxy-octane-1-nitrile having the following formula:—



Other aspects of the present invention provide a process for producing compound I and a process for producing 3,7-dimethyl-oct-2-ene-1-nitrile having the following formula:—



The compounds I and II—and more particularly compound II—possess a characteristically pleasant scent which enables them to be used as perfumes and for the formulation, in conjunction with other known compounds, of perfumed mixtures which can be used for soaps, cosmetics and deodorants. In this sense, they can replace with advantage, 3,7-dimethyl-octa-2,6-diene-1-nitrile (III):

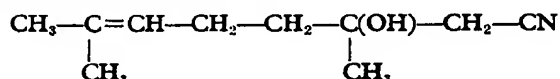


which is known as geranonitrile, in comparison with which they have a sweeter fragrance and an improved chemical stability.

In this connection, it should be noticed that, whereas geranonitrile, upon treatment for a few days at room temperature with a mixture of 98% H₂SO₄ and glacial CH₃COOH in the volume proportions of 5 to 25 gives rise, upon addition of water, to a slightly volatile pitchy substance, compound (II), which is saturated at the 6- and 7-positions, remains unaltered.

Another important application of compounds I and II is their use as intermediates in a number of organic syntheses.

Compounds I and II can be produced by using as the starting material, 3,7-dimethyl-3-hydroxy-oct-6-ene-1-nitrile (IV):



Compound IV can be obtained according to a synthesis disclosed in copending Patent Application No. 41876/75 (Serial No. 1,494,939).

Thus compound I can be produced by hydrogenation of compound IV, and compound II can be produced by dehydration of compound I.

The following Examples illustrate the present invention.

EXAMPLE 1

5.28 Grams of 3,7-dimethyl-3-hydroxy-oct-6-ene-1-nitrile (IV) in 25 ml hexane, supplemented by 0.52 gram of a catalyst comprising palladium on activated charcoal (containing 5% Pd by weight), were hydrogenated with stirring, in a glass apparatus, at room temperature, and under a hydrogen pressure of 760 ± 100 millimetres of mercury, absolute pressure.

The absorption of the stoichiometric amount of hydrogen to saturate the double bond of compound IV took about one hour.

After this time, the catalyst was filtered off and the solvent was evaporated under vacuum, and 3,7-dimethyl-3-hydroxy-octane-1-nitrile (I) was collected; the conversion and the selectivity with respect to compound I were both over 90%.

On subsequent distillation *in vacuo* with a Vigreux column, a product was obtained which has a purity of about 98% and a boiling point of 83°C — 84°C under an absolute pressure of 0.3 mmHg.

EXAMPLE 2

The compound I was obtained using the same ratio between the reactants as in Example 1, but by carrying out the hydrogenation in a steel autoclave under an initial hydrogen pressure of 8.6 kilograms per square centimetre (gauge). The procedures for collecting and purifying the product were very much the same as for Example 1.

EXAMPLE 3

2 Grams of 3,7-dimethyl-3-hydroxy-octane-1-nitrile (I) and 3 grams of basic Woelm aluminium oxide were maintained for 1.5 hours at 220°C — 230°C under a nitrogen stream in a glass flask equipped with a bubble condenser which was cooled with water.

After this stage, the mixture contents of the flask were allowed to cool to room temperature, then the reaction mass was taken up with diethyl ether and filtered, and the solvent was then thoroughly evaporated.

Thus, 3,7-dimethyl-oct-2-ene-1-nitrile (II) was obtained, which was composed of a mixture of the *cis*- and *trans*-isomers in a ratio of 45/55 approximately; the selectivity with respect to compound II was not less than 90%.

Compound II was obtained at a purity of 98% approx. by subjecting the residue as described hereinabove to distillation *in vacuo* and collecting the product which boiled at 52°C — 53°C under an absolute pressure of 0.1 mmHg.

The characterization of compounds I and II was effected by IR, NMR and mass-spectrography analyses.

The IR spectrum confirmed the presence of the following functional groups:

—OH	3460 cm^{-1}	} for compound (I)
—C≡N (non conj.)	2252 cm^{-1}	
—C—O of a tert.alcohol	1153 cm^{-1}	
=C—H	3045 cm^{-1}	} for compound (II)
—C≡N (conj. at alpha)	2215 cm^{-1}	
C=C (conj.)	1630 cm^{-1}	
=C—H (stretching)	700 cm^{-1}	

The NMR analysis (solvent CCl_4 , internal standard hexamethyldisiloxane HMDS)) indicated the following characteristic signals:—

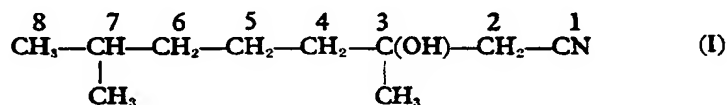
—OH	3.23 parts per million (ppm)	} for compound (I)
—C ₂ —(2)	2.42 ppm	
—CH ₂ —(4)	1.45 pm	
—CH		
—CH ₃		
—CH ₂ —(5,6)	1.24 ppm	}
CH ₃		
C	0.83 ppm	
CH ₃		

5	$\begin{array}{l} =\text{CH} \\ -\text{CH}_2-(4) \\ -\text{CH}_3 \text{ (cis- or trans-)} \\ -\text{CH}_3 \text{ (trans- or cis-)} \\ -\text{CH}_2-(6) \\ -\text{CH}_2-(5) \\ -\text{CH} \end{array}$	$\begin{array}{l} 5.03 \text{ ppm} \\ 2.08 \text{ ppm} \\ 1.98 \text{ ppm} \\ 1.85 \text{ ppm} \\ 1.50 \text{ ppm} \\ 1.20 \text{ ppm} \end{array}$	} for the compound (II)	5
	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$	0.81 ppm		

10 Mass spectrometry confirmed the molecular weights (169 for I and 151 for II) and the respective expected structures. 10

WHAT WE CLAIM IS:—

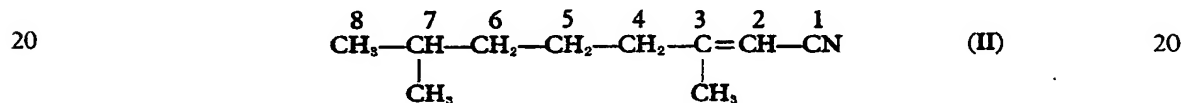
1. 3,7-Dimethyl-3-hydroxy-octane-1-nitrile having the following formula:—



15 2. A process for producing the compound claimed in claim 1, which comprises hydrogenating 3,7-dimethyl-3-hydroxy-oct-6-enitrile with hydrogen. 15

3. A process according to claim 2, substantially as described in the foregoing Example 1 or 2.

4. A process for producing 3,7-dimethyl-oct-2-ene-1-nitrile having the following formula:—



which process comprises dehydrating the compound claimed in claim 1.

5. A process according to claim 4, substantially as described in the foregoing Example 3.

25 6. 3,7-Dimethyl-oct-2-ene-1-nitrile whenever produced by a process according to claim 4 or 5. 25

HASELTINE LAKE & CO.,
Chartered Patent Agents,
28 Southampton Buildings,
Chancery Lane,
London, WC2A 1AT,
and
Temple Gate House,
Temple Gate,
Bristol, BS1 6PT,
also
9 Park Square,
Leeds, LS1 2LH.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

